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Hydrocarbon Molecules with Novel Structure: the First Fullerene Derivative Having a Fulvene-Type π -System and Polycyclic Aromatics Having σ - π Conjugation

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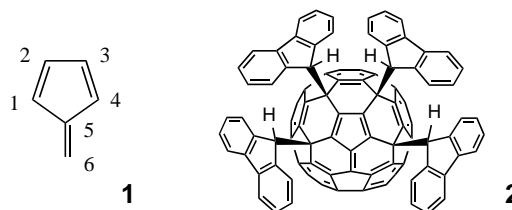
A spacious π -conjugated carbanion such as fluorenyl anion was found to add to fullerene C_{60} with high positional selectivity to afford the first tetrakisadduct of C_{60} having a fulvene-type π -electronic system on its spherical surface. This derivative reacts with various carbon nucleophiles at the fulvene's "exocyclic" sp^2 carbon to give the corresponding cyclopentadienide ion. Also synthesized were the polycyclic aromatic hydrocarbons fully annelated with a rigid bicyclic framework, i.e. bicyclo[2.2.2]octene. These planar polycyclic systems are characterized by the high oxidizability affording stable cation radicals and dications.

Keywords: C_{60} / π -conjugation / electrochemistry / [4+2] cycloaddition / carbanion / cation radical

1. The First Tetrakisadduct of Fullerene C_{60} Having a Fulvene-Type π -System on the Spherical Surface [1].

Fulvene (**1**) is a polarized cross-conjugated π -system, which reacts with nucleophiles selectively at the exocyclic sp^2 carbon to generate a cyclopentadienide ion. It is of great interest to construct such a π -system on the spherical surface of the fullerene molecule.

The reaction of C_{60} with an excess amount of potassium fluorenyl (3 equiv) in THF for 72 h under argon (*but without rigorous exclusion of air*) afforded tetrakis-(9-fluorenyl)adduct **2** as a black powder in 40% yield. The results of X-ray crystallography of **2** (Figure 1) clearly indicated that the four sp^2 carbons (C-1 – C-4) of



the fulvene structure are isolated from the outer rim π -conjugated system by four sp^3 carbons each bearing a fluorenyl group and that there is considerable bond alternation comparable to that in the previously reported planar fulvene derivatives.

Compound **2** reacts with various carbon nucleophiles selectively at the C-6 carbon to give stable cyclopenta-

ORGANIC MATERIALS CHEMISTRY —High-Pressure Organic Chemistry—

Scope of Research

Fundamental studies are being made for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic π -systems; chemical transformation of fullerene C_{60} ; utilization of carbon monoxide and dioxide for organic synthesis under the transition-metal catalysis.



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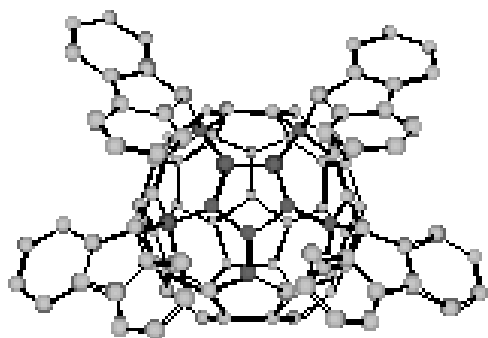


Figure 1. Molecular structure of **2** determined by Dr. M. Shiro of Rigaku Corp. The fulvenyl carbons and sp^3 carbons on the C_{60} cage are darkened for comprehensibility.

dienide ions. Of particular interest is the pentakis(9-fluorenyl)adduct **3**, which has the C_5 symmetric structure with the five spacious fluorenyl groups arrayed in a propeller-like arrangement (Figure 2). This anion undergoes a reversible one-electron oxidation to give a stable radical as shown by cyclic voltammetry and ESR experiments.

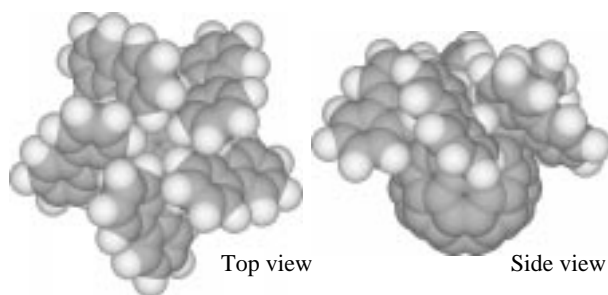
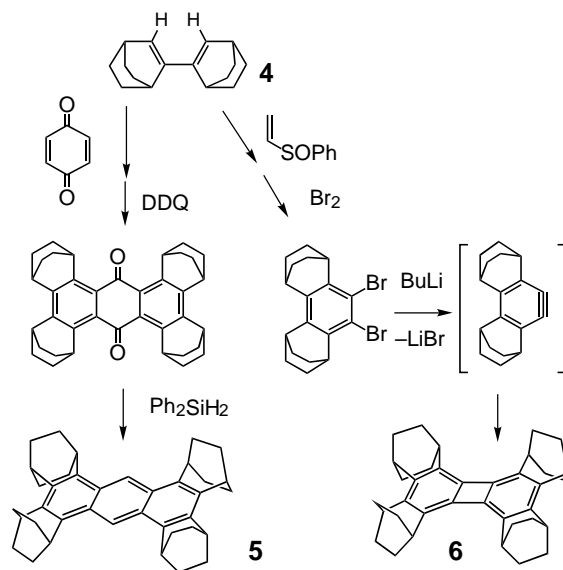


Figure 2. Space-filling representation of the AM1-optimized structure of **3**.

2. Synthesis, Structure, and Oxidizability of Polycyclic Aromatic Hydrocarbons Surrounded by Rigid Bicyclic Frameworks [2, 3].

In our previous studies, annelation with rigid bicyclic frameworks such as bicyclo[2.2.2]octene (abbreviated as BCO) was shown to be effective in stabilization of the positively charged, cyclic π -conjugated systems [4]. It is assumed that the rigidly held σ -bonds in the BCO unit exert not only the inductive effect but the σ - π conjugative (C-C conjugative) effect so that the HOMO levels of the π -system are raised.

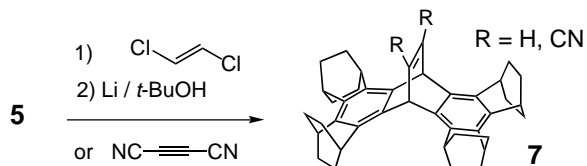
Thus, the BCO dimer **4** exhibited high reactivity as a diene to give various [4+2] cycloadducts, which can be transformed, for example, into representative polycyclic benzenoid aromatics with 14 and 12 π -electrons, anthracene **5** and biphenylene **6**, as shown in Scheme 1.



Scheme 1

In accord with the expectation, hydrocarbons **5** and **6** were characterized by the remarkably low oxidation potentials to generate the stable cation radicals ($E_{1/2} +0.21$ and $+0.33$ V vs Fc/Fc^+) and less stable dications ($E_{pa} +0.87$ and $+1.03$ V). Chemical oxidation with $NO^+BF_4^-$ afforded the stable cation radical **5** $^{\cdot+}$ (red-violet) and **6** $^{\cdot+}$ (blue-violet) as the BF_4^- salts, the dichloromethane solutions of which exhibited the triplet and 9-line ESR spectra respectively.

The chemical two-electron oxidation of anthracene **5** readily proceeded by the use of SbF_5 to give the blue-colored solution of dication **5** $^{2+}$, which was identified by both 1H and ^{13}C NMR measurements. Elevation of the HOMO level of **5** was also demonstrated by its high reactivity as diene in the [4+2] reaction with various dienophiles affording the dibenzobarrelene derivatives **7** (Scheme 2). Studies are now under way to investigate the unique electronic properties of **7** and to extend this methodology for the synthesis of the corresponding triptycene derivative.



Scheme 2

References

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